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ZERO-VOC WATERBORNE POLYURETHANE TOPCOAT

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Organic topcoats are the primary source of barrier-type protection against environmental degradation for Navy aircraft. In addition, these materials provide passive countermeasures against many enemy threats. Unlike other DOD applications, Naval aviation topcoats must provide superior protection with a thin barrier as to minimize weight for proper payload or operations. These coatings contain high volatile organic compound (VOC) contents; VOCs are released during painting operations as hazardous air pollutants (HAPs). This new topcoat incorporates resins based on novel polymer chemistries into its formulation. These resins are water-dispersible; no organic solvents are necessary for viscosity reduction and subsequent spray application. Successful implementation of this material would result in the elimination of VOC emissions during the topcoating process. Laboratory results indicate that coatings formulated with this novel technology are feasible and these systems meet or exceed the majority of specification requirements and field demonstrations are in progress. The alternative to low/no VOC materials is the implementation of expensive emission control equipment on facilities where painting operations are performed. If no actions are taken or delayed, the risk of falling out of compliance with federal, state, and local regulations becomes high. Non-compliance will result in fines, forced implementation of pollution-abatement equipment, and aircraft down time.

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1. INTRODUCTION

Coating systems on Navy aircraft perform a wide variety of functions. They provide desired optical effects (i.e., aesthetics, camouflage), corrosion prevention, erosion control, markings, electrical grounding, electromagnetic shielding, as well as other specialized properties. Clearly, their most critical contribution is the protection of materials and structures from corrosion and other forms of environmental degradation. An Air Force study (1) concluded that, "The rate controlling parameter for the corrosion of aircraft alloys, excluding the mechanical damage factor, is the degradation time of the protective coating system." These coatings protect not only metallic alloys from corrosion, but also plastics and polymeric composites from various degradation mechanisms (2). Specifically, Navy aircraft are deployed at coastal land bases or onboard aircraft carriers. The continuous proximity to salt water and high humidity combined with atmospheric impurities cause one of the most corrosive natural environments. In addition, many operational and maintenance chemicals commonly used or found on aircraft, such as paint strippers, battery acid, de-icing fluids, and cleaners, are corrosive. These effects are exaggerated even more so with aging fleet aircraft that have flown many flights over long periods of time, adding fatigue as another factor. Considering the high cost of these aircraft, in addition to fewer numbers of new aircraft programs, aircraft materials protection is of the utmost importance.

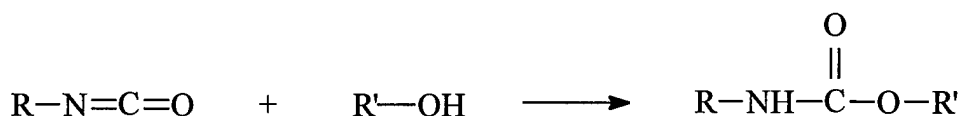
The most common organic coating system applied to the exterior surfaces of Navy aircraft consists of an inorganic pretreatment, an epoxy primer, and a polyurethane topcoat. In addition to this primer and topcoat paint system, other technologies have been introduced such as flexible primers and self-priming topcoats. These coating systems have protected aircraft structures from the frequently harsh operational environment due to their exceptional corrosion inhibition, adhesion, and durability characteristics.

Unfortunately, these coating systems have also been identified as a major contributor to the generation of hazardous materials and hazardous waste for the Navy (3). Recently, changes in coating composition and application procedures have occurred because of these concerns for environmental protection and worker safety. Many of these coatings have contained high levels of volatile organic compounds (VOC) as solvents and plasticizers, and heavy metal compounds as corrosion inhibitors and colorants. These ingredients are being severely regulated and coating formulations are being drastically changed accordingly. These environmental issues have created a drive toward coatings with ultra low (possibly zero) concentrations of VOC and non-toxic corrosion inhibitors.

The focus of this paper is the development of a zero-VOC waterborne polyurethane topcoat for Naval aviation applications. These systems eliminate VOCs, HAPs, and the need for pollution abatement equipment in painting facilities. Laboratory results indicate that the coatings perform as well as the present high-solids solventborne polyurethane and field demonstrations have commenced on aircraft sections as well as support equipment.

2. STANDARD TOPCOATS

A high-performance topcoat, conforming to MIL-PRF-85285, "Coating: Polyurethane, High Solids," is applied to Navy aircraft in order to enhance protection against the operational environment and to provide desired optical properties. Aliphatic polyurethane coatings are ideal for this application due to their superior weather and chemical resistance, durability, and flexibility. These urethanes are two-component reactive materials. One component of the coating is a polyisocyanate resin or an isocyanate-terminated prepolymer based on hexamethylene diisocyanate (HDI). The second component contains hydroxylated polyester. Upon mixing, the isocyanate groups react with the hydroxyl groups of the polyester:



The resulting polymer is flexible yet extremely durable and chemical resistant. Aliphatic isocyanates and polyesters are used in topcoats because they provide outstanding weather resistance compared to epoxies, whose aromatic groups degrade when exposed to ultraviolet light. References (4-7) provide more detailed discussions about polyurethane chemistry.

When the two components are combined and the polyurethane reaction begins, the coating is ready for application (i.e. no induction time is required). This coating is normally spray-applied to a dry film thickness of 50.8 ± 7.6 micrometers (2.0 ± 0.3 mils). The typical topcoat is set-to-touch and dry-hard (when cured at room temperature) within 2 and 8 hours, respectively. Although the painted surface can be handled after 6 hours without damage to the coating, full performance properties are normally not obtained until approximately 7-14 days.

The most critical performance requirements for topcoats are weather resistance, chemical resistance, and flexibility. Weather resistance is evaluated by laboratory exposure in an accelerated weathering chamber (8) for 500 hours. This chamber is a continuous cycle of high intensity ultraviolet light (xenon arc) and water spray. Although studies have shown that there is no precise correlation with outdoor exposure (9-11), the accelerated exposure does indicate if the coating is susceptible to ultraviolet and/or water degradation. These results are used in conjunction with actual outdoor exposure for 1 year. Both accelerated and real-time weathering conditions cause only minimal changes in the color, gloss, and flexibility of high performance aircraft topcoats.

Chemical stability is evaluated by exposure of the applied topcoats to various operational fluids such as lubricating oil, hydraulic fluid, and jet fuel at elevated temperatures and/or extended durations. Aerospace topcoats are also subjected to a dry heat of 121°C (250°F) for one hour. Suitable topcoats show no defects other than slight discoloration after exposure to these conditions.

Flexibility requirements for polyurethane topcoats include impact and mandrel bend tests. For high-gloss colors, a 40% elongation of the coating after impact at room temperature and a 180°

bend around a 2.54 cm (1.0 in) cylindrical mandrel at -51°C (-60°F) are required without cracking of the film. Flexibility requirements for low-gloss colors are less stringent at low temperatures because it is difficult to formulate flexible low-gloss coatings due to high pigment concentrations. A high pigment concentration normally embrittles the film.

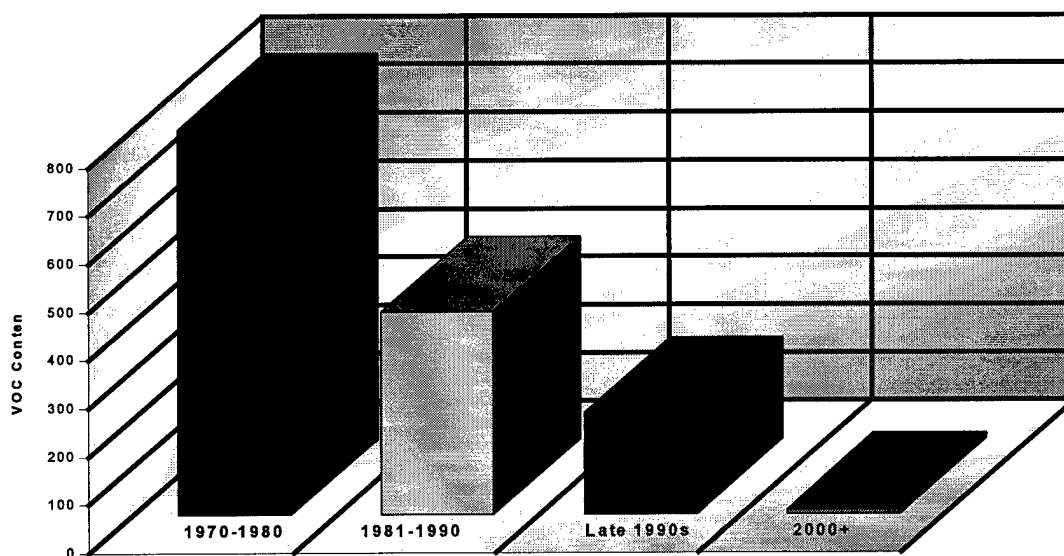
Another topcoat system applied to some Navy aircraft is the self-priming topcoat (SPT). SPT is a VOC compliant, non-lead, non-chromated, high-solids polyurethane coating that was designed to replace the current primer and topcoat paint system used on aircraft (12). This technology conforms to TT-P-2756, "Polyurethane Coating: Self-Priming Topcoat, Low Volatile Organic Compounds (VOC)." The SPT possesses the adhesion and corrosion inhibition properties of a primer as well as the durability and optical properties of a topcoat. The SPT effectively eliminates the need for a primer and thus eliminates the application manpower, time, and materials. In addition, the hazardous emissions and toxic wastes that are associated with current aerospace primers are eliminated. However, the SPT has exhibited more sensitivity to processing (surface preparation, pretreatment, etc.) than the standard coating systems. These properties are most likely due to its lower solvent content in conjunction with the reduced adhesion associated with applying a urethane system directly to a pretreated metal substrate. The specified thickness of this film is 50.8 to 66.0 micrometers (2.0 to 2.6 mils). SPTs have been successfully applied to a full variety of operational Navy aircraft (e.g., F-14, F-18, AV-8, H-3, H-46, P-3). Research and development at the Naval Air Warfare Center Aircraft Division in Patuxent River, MD (NAWCADPAX) is in progress to reduce the VOC content of SPTs until the ultimate goal of zero is attained.

3. COMPLIANT COATINGS ISSUES AND ZERO VOC

3.1 Environmental Regulations And Hazardous Materials As the environmental consciousness of the world continues to increase, more efforts are being devoted to finding safe, compliant solutions to past, current, and future environmental problems. One major factor affecting the Naval Aviation in recent years, has been the Clean Air Act Amendment (CAAA) of 1990. This law significantly affects the type of materials and processes that will be approved for use in the future. In response to this situation, the Navy has expanded its efforts to reduce the amounts of hazardous materials generated from the cleaning, pretreating, plating, painting, and paint-removal processes used in both production and maintenance operations. The materials associated with these processes have been identified as major sources of hazardous waste by the EPA (13). Specifically, numerous research and development efforts have been established to address the environmental concerns with organic coatings. These environmental efforts can be described by two main thrusts: the development of low volatile organic compound (VOC) coatings and the development of non-toxic inhibited coatings. The development of non-toxic inhibited coatings is concerned with eliminating toxic heavy metal pigments, such as lead, chromates and cadmium, used in protective primers and topcoats. The efforts in low VOC are

aimed at reducing the volatile organic compound content of aircraft coatings to meet environmental regulations, especially the state of California's Air Quality Management Districts (AQMD) rules and the CAAA Control Techniques Guideline (CTG) for the aerospace industry (one of 174 source categories); the zero-VOC topcoat is one such effort.

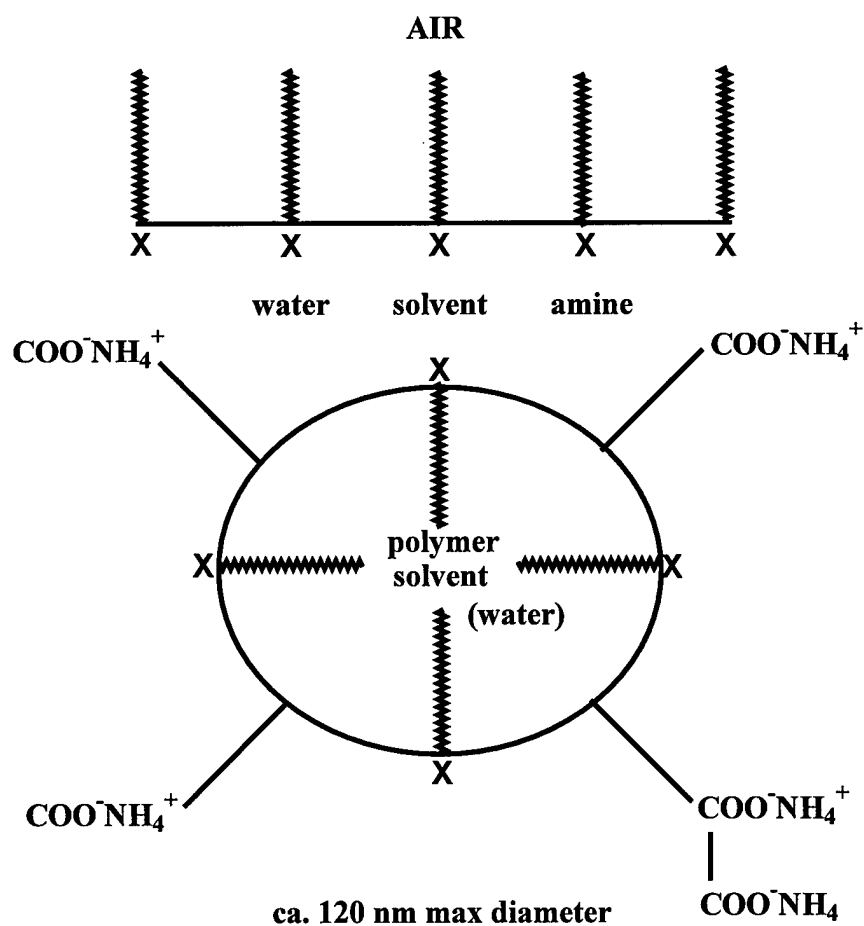
Low VOC versions of the standard military aircraft primers and topcoats have already been developed to comply with the CAAA Aerospace CTG. These materials are based on waterborne and high solids. New resin and additive chemistries have brought VOC contents even lower as the twentieth century comes to a close. The chart below summarizes the VOC content of coatings for past, present, and future systems. Exempt solvents technology, while solving a VOC problem in most cases, creates an ozone depleting chemical problem and is no longer perceived as a potential technology solution.



3.2 Waterborne Technology Water has long been used as a carrier for organic coatings. The polymers for these coatings are usually modified with hydrophilic groups and dispersed in water to form either solutions or emulsions. Most latex paints are based on thermoplastic resins that are suspended in water to form spherical particles. These particles, whether pigmented or neat, are usually covered with a thin layer of emulsifier to maintain a stable dispersion. When applied to a surface, these spheres coalesce into a continuous film as the water of the emulsion coating evaporates. This film formation mechanism tends to lead to longer drying times in high humidity environments. Other effects of using water as the diluent include: smoother surface finishes due to greater flow times, less overspray when using air application equipment (due to the higher density of water), and easier clean up (usually accomplished with soap and water).

Unfortunately, these coatings have some disadvantages. For example, they are more sensitive to surface contamination, like oils and greases. Also, these films tend to be porous and their high affinity for water can lead to poor resistance in moisture environments resulting in coating failure when wet, or exposed to high humidity conditions.

Waterborne or water-reducible, high-performance coatings are unique in the way that they contain resins that are usually not soluble in water. The resin exists in its own micellar phase. The figure below illustrates the resin micelle in a waterborne coating. As shown in the figure below, neutralized carboxylic groups and surfactants stabilize the particle. Excess amine and solvent distribute between the phases. Because the polymer exists in its own organic phase surrounded by water, the solvent distributes between the organic phase and the aqueous phase. This solvent, called the coalescing solvent or co-solvent, aids in film formation as the water evaporates by allowing binder and pigment particles to fuse in a continuous film (14). Because water is used as the primary liquid medium or as a diluent, formulations based on waterborne resins have much lower VOC levels than their solventborne counterparts. Recent advances in urethane and additive chemistries have shown that coatings approaching zero VOC are feasible, consisting of low viscosity, water-soluble reactants (15).



Polyurethane coatings comprise an area where high performance waterborne coatings have been investigated. One-component polyurethane dispersions have been in existence for some time and generally consist of fully reacted polyurethane resins which are predominately thermoplastic. Since urethanes are not readily compatible with water, these systems are modified ionically and non-ionically with hydrophilic groups to aid in the stability of the dispersions. After application, these films form by the coalescence of the long chain urethanes. Although some work has been performed to investigate ways of crosslinking these systems, they tend to have lower crosslink densities and are not as chemically resistant as their solventborne counterparts.

Recently, resin manufacturers have shown signs of success in working with two component water based polyurethane resins for high performance coatings. One example is based on an aliphatic polyol prepolymer and a polyisocyanate. The polyols are pre-reacted with a diisocyanate and emulsifying agents to form a linear hydroxy-terminated prepolymer. The hydroxy-functional groups aid in the stabilization of the polyurethane dispersion. In addition, a water dispersible polyisocyanate has been synthesized which has a preferential affinity for the polyol over the water competitor. The two components are mixed with an excess of isocyanate to form the final high-performance polyurethane product. Government laboratories and the commercial resin industry are investigating other variations on water-based urethane chemistry and coating manufacturers have begun to formulate finished products from this technology. For example, the Army is currently investigating a water-reducible chemical agent-resistant coating (CARC) under the Strategic Environmental Research and Development Program (SERDP) with multi-service participation.

3.3 The Zero-VOC Topcoat A zero-VOC topcoat has been developed under a joint Navy-industry effort funded by SERDP (PP-65). This topcoat, formulated by Deft Coatings, Inc., is based on a novel urethane chemistry that requires no co-solvent. Through manipulation of the polymer backbone chemistry and the evolution of new surface-active and rheological additives, a water-reducible polyurethane binder system was developed that contains no organic solvents and emits no hazardous air pollutants (HAPs). The zero-VOC topcoat offers the potential for the DOD to go beyond environmental compliance in its painting operations.

After achieving "Proof of Principle" for zero-VOC coating technology under SERDP, the project transitioned to the Environmental Security Technology Certification Program (ESTCP) whose office funded NAWCADPAX to demonstrate and validate the topcoat for use on military aircraft. Successful implementation of this topcoat would result in the elimination of approximately 120 tons of VOCs per year based on GSA estimates of MIL-PRF-85285 usage throughout the DOD. The primary objective of this ESTCP-sponsored project is twofold: to eliminate hazardous materials and VOCs in the topcoating process and to maintain the high-performance characteristics found in the current VOC-containing topcoats.

A joint group led by NAWCADPAX and consisting of technical representatives from the Naval Aviation Depots at Jacksonville, FL; Cherry Point, NC; and North Island, CA; Warner-Robins Air Logistics Center; and other government agencies reached technical consensus on engineering, performance, and testing requirements for topcoats. The joint group defined critical

tests with procedures, methodologies, and acceptance criteria to qualify alternatives against these technical requirements. This joint test protocol (JTP), developed for the ESTCP (Project No. 199802), is currently being used to evaluate the current candidate topcoat and will be employed in evaluations of future candidates. The JTP contains two sets of requirements and tests. The first summarizes a common set of requirements and tests agreed upon by the joint group. Some of these requirements (and associated tests) include adhesion, weatherability, cleanability, fluid resistance, flexibility, and viscosity. The second includes program-specific, or "extended," requirements and tests identified by at least one of the affected programs. Examples of these extended requirements (and associated tests) are chemical agent resistance, corrosion resistance, more stringent tests for cleanability and flexibility, and signature issues.

The earliest versions of the zero-VOC topcoat experienced poor drying characteristics, including leveling, gloss, flexibility, and use time (pot life). New dispersing agents and rheology additives were able to rectify the majority of the problems; however, at this time, it appears that a property trade-off situation exists between pot life and flexibility. The latest two versions of the topcoat (camouflage gray) each exhibit a shortcoming in one of the two properties. One version passes all flexibility requirements, but has a pot life of three hours (one hour short of requirement); the other passes the pot life requirement, but displays a GE impact flexibility of 20% (40% required) at ambient conditions. Both versions demonstrate excellent low-temperature flexibility: no cracking was observed when coated panels were bent over a 1/2" cylindrical mandrel at -60°F.

Two solutions were proposed. The first involves optimizing the formulation to achieve the best results in both pot life and flexibility. The second solution involves using plural-component spray equipment. With plural-component spraying, both components (see under Section 2 on p.3) are placed in separate material-storing compartments. Hoses lead from each compartment to a "mixing area". The mixing area consists of a network of intertwining tubes that blend the components. The admixed coating exits the mixing area and proceeds directly to the spray gun's nozzle. Therefore, excess waste is eliminated because only the amount used is admixed. Also, pot life is not an issue because the admixed material is applied seconds after mixing.

Although the advantages of the plural-component spray equipment are significant, its use is not recommended here for the following reasons. Plural-component spray equipment exerts a high shear force on the mixture as it passes through the mixing area. Work at NAWCADPAX showed that when combining the components of the current zero-VOC coatings with high-shear (e.g. high-speed mixer), excess carbon dioxide bubbles were generated, resulting in a surface finish with bubbles. This phenomenon is observed when mixing waterborne polyurethane coatings in a similar manner; bubbles are not observed when mixing solventborne coating systems. The zero-VOC coating would have to be reformulated to be compatible with the new spray equipment. Also, the average plural-component spray unit can accommodate up to three spray guns. The largest aircraft painted by the Navy is the P-3 Orion, which requires eight painters, or three units. Because the units are on the order of \$40,000 each, a capital investment of \$120K per paint hangar would be necessary. Air Logistics Centers' investments would be even higher for sites that refinish large cargo aircraft such as the C-5. Because reformulation is

necessary to achieve either the required pot life or sprayability with plural component equipment, the more cost-effective route at this time is to pursue pot life extension.

Under ESTCP, technology demonstrations will be conducted at NADEPs in Jacksonville, FL; Cherry Point, NC; and North Island, CA. Throughout this two-year evaluation, several Navy aircraft will be painted with the zero-VOC topcoat at the Naval Aviation Depots (NADEPs). Periodic inspections for performance will be scheduled with NAWCADPAX and NADEP representatives present for evaluations and if reformulations may be necessary to maintain current standards. Additionally, Warner-Robins ALC has agreed to demonstrations on USAF weapon systems component parts. Aft engine cowlings were painted at Warner-Robins in October 1998 and have been exposed outdoors at that facility for one year. The cowlings are washed and rinsed every 60 days according to the T.O. 1-1-8 protocol. Assessments are made of topcoat degradation before and after all washings. Results after one year indicated that there were some cleanability issues with the formulation used, but damage severity associated with outdoor weathering was comparable to the standard MIL-PRF-85285 topcoat.

The zero-VOC topcoat will be substituted for the standard topcoat when the aircraft is scheduled for its final painting at the NADEP. Performance of the new material must, at a minimum, perform comparably to aircraft painted with the standard finishing system at approximately the same time frame. Based on the results of these demonstrations and meetings of the joint group, the JTP may be modified to reflect the optimized performance with regards to pot life and flexibility.

4. SUMMARY

Many new innovations in protective coatings technologies have emerged during the past few years, one of which is the zero-VOC topcoat. The use of a zero-VOC topcoat is expected to have several benefits that will be applicable to any DOD facility or subcontractor engaged in the painting of aircraft or ground support equipment. Some of the regulatory, economic, and readiness benefits include the following: avoidance of fines, avoidance of hard emission controls, reduced waste and disposal costs, improved work space/facility environment. Most importantly, because the elimination of compliance issues will not result in aircraft downtime, the Navy will be able to maintain its operational readiness.

5. ACKNOWLEDGMENTS

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